REMARKS

Applicants thank the Examiner for the allowance of claims 1-14, 16-24, 26 and 28-32 and indication of allowance of claim 56.

Applicants have corrected the obvious spelling errors in claims 21, 22, 53, and 54 and thank the Examiner for bringing them to the attention of applicants. New claims 61-64 are added. They are based on the teaching of printing an image on a 330 micrometer PVC sheet. Claims 21, 22, 53 and 54 are amended to take into account the observations of the Examiner that some terms were misspelled. Applicants submit that these changes are cosmetic in nature.

The application now contains claims 1-24, 26, 28-57 and 60-64.

Claims 15 and 47 stand rejected under 35 U.S.C. §112, second paragraph as being indefinite. Applicants disagree. It is well known that some silica materials bond to polymers, if present during polymerization. This is described, *inter alia* in a paper that was published, at some unknown date, after the filing date of the present application, in the international phase. This dating of the reference is based on the dates of the references, the latest of which is dated 2000. This paper clearly states that at over 15% silica particles for Highlink OG materials (one of the materials mentioned), a strong interaction occurs at the polymer-silica interface. While this paper is not prior art, it is attached hereto (without mention on a Form PTO-1449) to explain the phenomena, which the Examiner questioned.

Claims 33-46, 48-55, 57 and 60 stand rejected under 35 U.S.C. §103(a) as being unpatentable over Ichiro. Applicants respectfully traverse the rejection and submit that it does not provide a *prima facie* case of obviousness. Applicants enclose a machine translation of the patent from the JPO web site. However, applicants are still confused as to the exact meaning of the specification, which is not surprising in such machine translations from Japanese. A Form PTO-1449 reporting this submission is attached hereto. Applicants respectfully request that the item listed thereon be initialed by the Examiner to ensure that it appears on the face of the patent issuing on the present application. Applicants assume that the art has already been considered by the Examiner in accordance with MPEP §1893.03.

Applicants note that both the rejection and the following remarks are based on the abstract supplied by the Examiner with the rejection and, to the extent possible, to the translation of the specification. Applicants note that the Examiner has available to him an "oral translation" service (in addition to other such translation services), so that any lack of clarity in the translation can be easily cleared up.

Ichiro describes an ultraviolet curable resin material for coating a molding that may contain substantial amounts of colloidal silica. The use described in the disclosure is for coating

automotive parts and other products so that they weather well (see par 0046). However, this reference teaches nothing with respect to the claims rejected as being obvious in view of the reference.

The methods of coating used are described at par 0042. None of these are generally used in coating sheets of material for printing.

The only possibility of a rejection on obviousness would be that it is obvious to coat the coating of Ichiro onto a sheet of polymer.

Claim 33, the only independent claim in the group includes two elements. The first of these is "a sheet of polymer". There is no teaching in Ichiro that the molding resin should be used to coat a sheet of polymer. Coating such a sheet would not be obvious in view of the stated utility of the Ichiro reference. Applicants submit that, given the very large numbers of teachings in the prior art of coatings of all kinds, it would not have been obvious for a person of the art to look to art in the field of protective coatings, against abrasion and weathering, for a coating to use on printable sheets.

The second limitation is "a *printable* coating in the form of a *film,* on the polymer sheet comprising at least 25% nano-silica."

The Examiner indicates that the material disclosed in Ichiro is inherently printable. The reference does not teach that the material is printable. The mere presence of silica might not be enough to provide a printable surface. This is especially true since at least one constituent; the urethane constituent, is generally not readily printable.

Furthermore, applicants submit that the maximum amount of silica in the total coating is unclear. However, an attempt is made to determine the maximum percentage of silica based on the recommended ranges given.

The maximum *recommended* (by Ichiro) amount of silica is 60/160 or 37.5% of the total of monomer and silica, without the other additives, (par 0029). The additives are *recommended* to be 5-20 parts of the monomer amount (par 0034), 1-5 parts of the monomer amount (par 0036) and 1-6 parts (par 0038). Overall, the maximum percentage of silica in the recommended range would then be 60/(100+60+5+1+1)=60/167=35.9%.

Thus, for the use described, namely, the covering of rigid objects the maximum recommended is just over 35%. However, even if it were taught to use the general formulation of Ichiro, the person of the art would not use this *maximum* recommended silica formulation especially for coating of printing substrates. Firstly, as stated at par 0029, as the amount of silica increases, the chances of cracks is increased. For coating a flexible surface, this problem is exacerbated as is the problem of adhesion mentioned in the same paragraph. Thus, a person of

skill in the art would probably avoid using the upper end of the recommended range. Rather, he could more likely be expected to use the middle of the range, namely 35 parts per 100 of monomer. This would result in a silica percentage of only 35/142=24.6%. Furthermore, since the amount of abrasion protection required on a polymer sheet would be far lower than that on an automotive headlight, the person of skill in the art would be led to use lower percentages of silica to avoid the problems described, since the full abrasion protection of the Ichiro material would not be considered to be necessary.

In summary, applicants submit that:

1) A person of ordinary skill in the art would not use an abrasive protection resin for coating a sheet with a film. There is no reason given for doing so and no stated need for the protection given.

2) Even were a person of the art to consider, for some reason, that it is desirable to coat a polymer sheet with a compound according to Ichiro, there is no reason to expect that the maximum recommended amount of silica would be used. In fact, it is reasonable to believe that the coating would be made with less silica, since sheet material is usually subjected to lower environmental stress than the headlights which are the main use described in Ichiro. It would be expected that he would use less than 25% silica in the formulation.

3) Even were one to agree that the person of skill in the art would, in fact, utilize the maximum recommended amounts of silica in coating a sheet, there is no proof that the coating would be printable, as claimed in claim 33, since the Ichiro coating contains a substantial amount of urethane. In fact, it appears that the material as a whole is considered by Ichiro as being a polyfunctional urethane acrylate (par 0009).

In addition, the Examiner will note that many of the dependent claims distinguish over this art. For example, the maximum amount of colloidal silica in the recommended amounts appears to be under 40%. Thus, (even if all the above arguments are not accepted) at least claims 39-41 have larger percentages of silica than the reference. Furthermore, there does not appear to be any teaching of an amine anchorage agent as defined in claims 49-54.

In view of the above amendments and remarks, applicants submit that the claims are all patentable and that the application is ready for allowance.

Respectfully submitted,
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Use of Colloidal Silica Acrylates in UV coatings - Impact of Size, Size Distribution and Silica Loading on Film Properties.

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Abstract

We investigated in this work the impact of particle size, size distribution, and silica loading on film properties of UV-cured hybrid organic-inorganic thin coatings. Commercial silica organols of hexanediol diacrylate monomer (HDDA) containing monodisperse silica nanospheres (13, 25 and 50 nanometers) were mixed with a polyester tetraacrylate (PEA) to give coatings with controlled particle size distribution and silica loading (0 to 40%).

Dynamic mechanical thermal analysis (DMTA) measurements showed that complex modulus *(E*)* increased and loss tangent (tanδ) decreased with small particle size and high silica content, but the dynamic glass transition temperature *(Tg)* was unaffected by size and size distribution . Coatings with mixtures of 50 and 13 nm particles at 75/25 weight ratio obeyed to volume packing theory and gave the highest values of E* and tanδ. Resistance to abrasion and friction were more effective with 50 nm particles, while gloss was highest with 13 nm particles. These properties were best seen when silica content is superior than 15 % where strong interactions at the silica-polymer interface and particle/particle were detected. AFM observation showed that the surface of the coating was well covered with silica particles, protecting it from aggressive physical and chemical attacks. In all cases, the properties of hybrid coatings were found superior to the pure organic coating.

Key words: acrylic colloidal silica, nanocomposite, nanofillers , UV-curing, size and size distribution, filler concentration, viscoelastic properties, friction, abrasion resistance, gloss.

INTRODUCTION

Hybrid organic-inorganic UV or EB cured coatings can be made with ready-to-use acrylic monomers or pre-polymers containing a high content of pre-dispersed silica nanospheres. Usage of such products have been described in literature, fulfilling protection requirements for wood, metal, glass, plastic substrates and fiber optics, mainly against abrasion, scratch, chemical wear and tear, and barrier to gas [1-6]. Two recent studies detailed the role played by silica particles in the enhancement of hardness, resistance to scratch and abrasion, to aggressive chemicals while maintaining transparency and gloss. The improvement was explained by the high surface covering by silica nanospheres and a homogeneous distribution in the bulk of the coatings [7-8]. Another work described the increase of the photo-curing rates of colloidal silica acrylates compared to the parent monomers.[9]. Polymerization kinetics.[10] and structure and morphology[11] of silica-filled poly(hydroxyethyl methacrylate) were also commented.

It is also well researched that the use of fillers would affect physical , chemical and electrical properties of the composites: stiffening, tensile strength, flexural strength, elongation, tear resistance, impact strength, hardness, friction coefficient ,abrasion resistance, rheology, resistance to corrosion, thermal expansion, electrical conductivity, dielectric constant [12]. It is also common in the industry to mix small to large particles to get desired properties such as solid content, viscosity, mechanical properties. Effects of size and size distribution of fillers on packing efficiency were studied by different authors. For spherical particles, the key parameters affecting packing density were volume and the size ratios of large to small particles. Maximum density was obtained when the small particles were packed to their maximum volume within the voids of the large spheres [13]. The effect of binary particle size blending on latex viscosity [14,15,16] or blending hard-soft latexes on film properties [17] was discussed. Results were explained in terms of packing efficiency.

In the field of UV-cured coatings, the effect of size, size distribution of inorganic nanofiller has not been yet concluded due to the fact that few commercial products with controlled size were proposed.

In this work, we investigated on thin UV-cured hybrid coatings the impact of size, size distribution and loading of silica nanoparticles on the dynamic mechanical properties, abrasion and scratch resistance, surface friction and gloss. Commercial grades of silica organosols (Highlink OG) in hexanediol diacrylate (HDDA, $Tg_{DMTA} \approx 100°C$) were mixed with a polyester tetraacrylate (PEA, $Tg_{DMTA} \approx 30°C$) to

give desired formulations. The organic composition was maintained constant (HDDA/PEA = 86/14 weight ratio). Particle size (13, 25, 50 nm), size distribution (mixtures of 13 and 50 nm particles), and silica loading (0 to 40% w/w) were the main parameters.

Details of the surface of the coatings were also observed using Atomic Force Microscopy (AFM).

EXPERIMENTAL

1. Materials
- Monomers:
  - Hexanediol diacrylate HDDA (UCB/Cray-Valley):
  - Polyester tetraacrylate EB 80 (UCB) labeled PEA in the text.
- Acrylic silica monomers: (Clariant)
  - Highlink OG103-31 (30% SiO2 in HDDA, particle diameter : Dp =13 nm)
  - Lab OG103-32 (30% SiO2 in HDDA, particle diameter : Dp =25 nm
  - Highlink OG103-53 (50% SiO2 in HDDA, particle diameter : Dp =50 nm)
- Photoinitiator: : Irgacure 184 and Darocur 1173 (Ciba Specialty Chemicals) used at 6.5% weight with respect to monomer
- Substrates: Opacity card F2C (Leneta); glass plates (Prodeco).
- UV curing: Fusion F300 unit ; H bulb(120 W/cm); 3 passes; conveyor speed : 6.5 m/min; air .

2. Tests
- Dynamic mechanical properties: DMTA MkIII (Rheometrics) single bending mode; 1Hz; strain 16 μm; heating -70 to 165°C, 4°C/min. Film preparation: Free films are drawn down over a glass plate and submitted to UV curing. The thin cured films are then peeled off from glass substrate and cut out for DMTA analysis. Film dimensions: LxWxT 15 x10 x 0.075 mm.
  Accuracy: Sd(LogE*)=0.05 Pa ; Sd(tanδ)= 0.002 ; Sd(Tg)= 2°C
- Abrasion: Digital Abraser 5131 (Taber) ; Wheels CS10 F; 500g load; 250 cycles.
- Reflection densitometer: RD 918-SB (MacBeth) ; Results expressed as
  % abrasion = [(O.D$_0$-O.D$_1$)/O.D$_0$]x100
  O.D$_0$ and O.D$_1$: optical density of coating before and after abrasion
- Friction: Thin film analyzer (Rhopoint Instruments)- steel ball probe
- Gloss at 60°: MicroTri Gloss (BYK Gardner).
- Atomic Force Microscopy NanoScope 3100 (Digital Instruments): Tapping mode –slope imaging- 2 x2 microns scan.
- Code : Si 25/D1:D3(1:3) means 25% SiO2 ; mixture 25 / 50 nm ; 1/3 weight ratio

RESULTS and DISCUSSION:

Aspect of the coating
All coatings prepared in this work are clear and transparent, showing good leveling and excellent adherence onto the Leneta plastic substrate.

1 **Particle size effect** *(table1)*

FORMULATION		Size (nm)	Standard	1	2	3
Code			Ref	SI 25/D1(1)	SI 25/D2(1)	SI 25/D3(1)
SiO$_2$	(% wt)		0	25	25	25
HDDA	(g)		86	--	--	35.9
PEA	(g)		14	10.4	10.4	10.4
HOG 103-31	(g)	13	--	89.6	--	--
Lab 103-32	(g)	25	--	--	89.6	--
HOG 103-53	(g)	50	--	--	--	53.7

Results		Standard	1	2	3
Log (E') (-50°C) Pa		9.09	9.04	9.08	9.09
Tg °C		86	84	87	88
Tan δ (at Tg)		0.127	0.114	0.118	0.122
Log (E'r) (150°c) Pa		8.06	8.24	8.18	8.15
Abrasion %		28	9	6	4
Gloss (60°)		85	84	80	77
Friction g.force		12.2	8.5	4.9	3.8

HDDA/PEA = 86/14; photo-initiators (2/5 Irgacure 184 + 3/5 Darocur 1173) at 6.5% with respect to monomers.

Table 1 : Formulation and coating properties – Effect of particle size

1-1   Surface characterization by AFM   (Figures 1a-1b-1c)

AFM observations of the coatings loaded with 25% silica show a close-packed organization of monodisperse silica nanoparticles covering the whole surface *(figure 1-a, 1-b, 1-c)*. AFM observation of the coating loaded with 50 nm particles *(fig 1-c)* shows a bumpy surface made of silica particles which are homogeneously distributed and well embodied in the polymer. The good particle dispersion indicates a good compatibility between inorganic-organic phases. One can notice that when coatings are filled with 13 nm particles, many small particles are detected, easily explained considering the relationship between N, the particle number and D the particle size: $[N1/N2 \propto (D2/D1)^3]$.
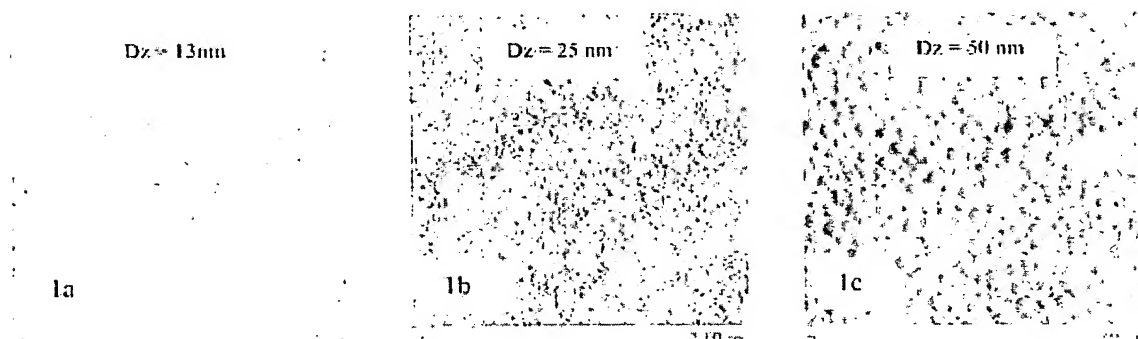

Figure 1   AFM analysis   1a) Coating Si 25/D1(1)   1b) Coating Si 25/D2(1)   1c) Coating Si 25/D3(1)

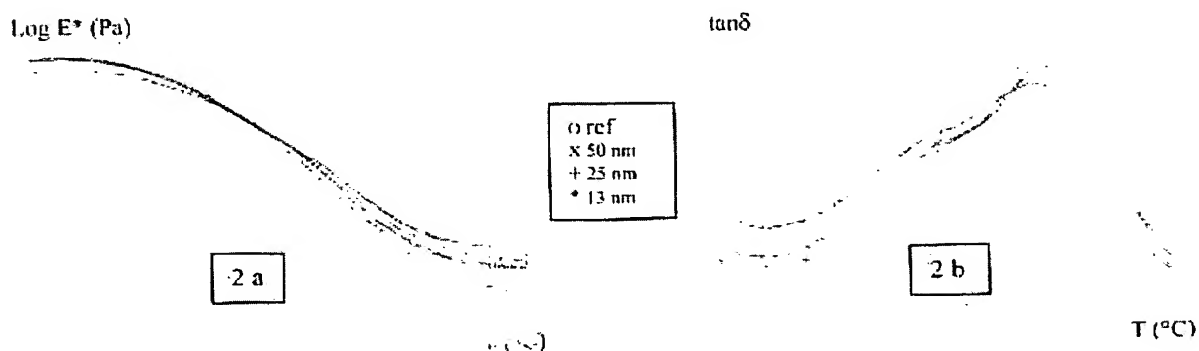### 1-2   Dynamic mechanical properties   (Figure 2)

Figure 2: Effect of particle size   2a) Log E* vs T   2b) tanδ vs T

DMTA is a precious tool to investigate bulk properties of solids. In *figure 2*, the logarithmic of complex modulus *(Log E*)* and loss tangent *(tanδ= E''/E'* : ratio of loss modulus E'' to elastic modulus E') are plotted against temperature for coatings filled with different silica particle size .

At −50°C, all coatings, being in the glassy state, are stiff and have similar $E^* \approx 10^9$ Pa,. E^* is not size dependent.

The effect of particle size and crosslinking on elastic modulus is better detected at the rubber plateau (150°C). Effectively, it is well known that the elastic modulus E^*_{rubber} is sensitive to crosslinking density [18,19,20] and to filler content [12,21]. We found the reinforcement of hybrid coatings higher than the cross-linked reference coating (0% SiO_2). This property is however less pronounced than with uncrosslinked coatings [11]. As the particle size gets smaller, we get larger values of E^*_{rubber}. The high contact area (50 to 200 m²/g) at the particle surface and interface favors strong interactions. This promotes good compatibility between the organic and inorganic components of the composite.

The dynamic glass transition temperatures Tg=88°C (at $tan\delta_{max}$) is not size dependent but higher than reference coating Tg_{ref}= 81°C. Harder coatings are therefore obtained.

The loss tangent is smallest with 13 nm particles ($tan\delta_{max}$= 0.11), and highest with the reference ($tan\delta_{max}$= 0.13). Elastic behavior is therefore more pronounced.

In summary, in comparison with the pure organic coating, the introduction of small nanoparticles is effective in reinforcing the stiffness of the composite by increasing E^*, enhancing elastic behavior by lowering $tan\delta_{max}$ and increasing moderately the Tg of the composite.

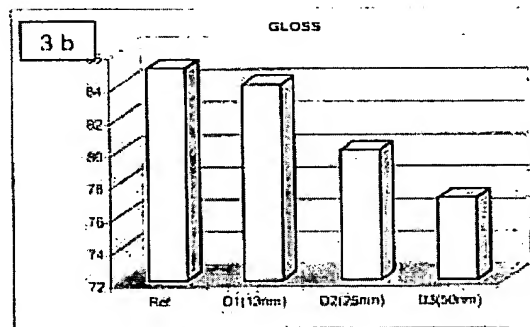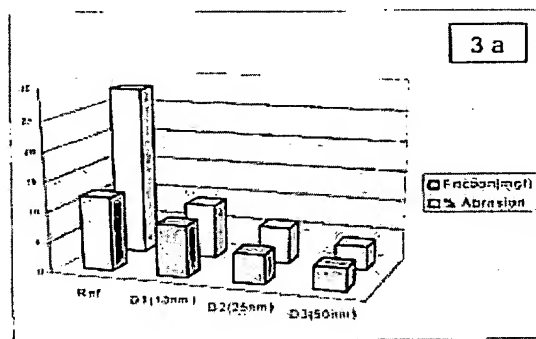**1-3   Abrasion resistance and friction** *(Figure 3 a)*

Figure 3: Effect of particle size *a) abrasion & friction b) gloss 60°*

When comparing the samples before and after being submitted to the Taber abrasion test, one can clearly see the interest of using pre-formed silica nanoparticles in high performance coatings *(table 1)*. While the reference coating is severely eroded (*abrasion*=28%), the hybrid coatings suffer 3 to 6 times less. An interesting result is that less abrasion is detected with 50nm particles (4%) than with the smaller 13nm particles (9%). This could be explained by looking once again at *photo 1-c*, where the bumpy surface of the coating loaded with 50 nm particles should offer less physical contact with the abrasion rolls during the experiment.

Friction coefficient can be efficiently and rapidly assessed with the TFA analyzer by measuring at steady state the angular deflection force of a pendulum moved across the coating. A steel ball probe is used and friction is the force registered at equilibrium. We can see that the friction decreases with larger particles and is well correlated with resistance to abrasion.

1-4   Gloss *(figure 3-b)*

Gloss is related to surface smoothness and surface leveling. The reference coating is very glossy (rating = 85) when measured at 60°. The coating loaded with 25% / 13 nm particles, is rated 84. This result shows that the very evenly dispersed small particles do not affect scattered light at the surface. Gloss decreases when larger particles are used.

2   Particle size distribution effect   (table 2)

Size distribution is easily controlled by blending different colloidal silica acrylates. In this work, we consider particles of 13 and 50 nm (D_{large}/D_{small} = 3.8). The coatings are loaded with 25% silica at various weight ratios :0 to 100%

FORMULATION *	11	12.	13	14	15	16
Code	Si 25/D1 (1)	Si25/D1:D3 (3:1)	Si25/D1:D3 (1:1)	Si25/D1:D3 (1:3)	Si25/D1:D3 (1:9)	Si 25/D3 (1)
SiO₂ (% wt)	25	25	25	25	25	25
HDDA (g)	—	9	17.9	26.9	32.2	35.9
PEA (g)	10.4	10.4	10.4	10.4	10.4	10.4
HOG 103-31 (g)	89.6	67.2	44.8	22.4	9	—
Lab 103-32 (g)	--	—	—	—	—	--
HOG 103-53 (g)	—	13.4	26.9	40.3	48.4	53.7
Results						
Log (E*) (-50°c) Pa	9.04	9.23	9.25	9.19	9.20	9.09
Tg °C	84	88	87	86	87	88
Tan δ (at Tg)	0.114	0.122	0.122	0.135	0.132	0.122
Log (E*r)(150°C) Pa	8.24	8.39	8.42	8.29	8.21	8.15
Gloss (60°)	84	81	79	81	76	77
Abrasion %	9	9	7	7	6	4

Table 2 : Formulation and coating properties – Effect of particle size distribution

2-1   Dynamic mechanical properties   (figure 4)

Log E* (Pa)   tanδ

- 50 nm
x 50/13 (3:1)
o 13 nm

4 a   4 b

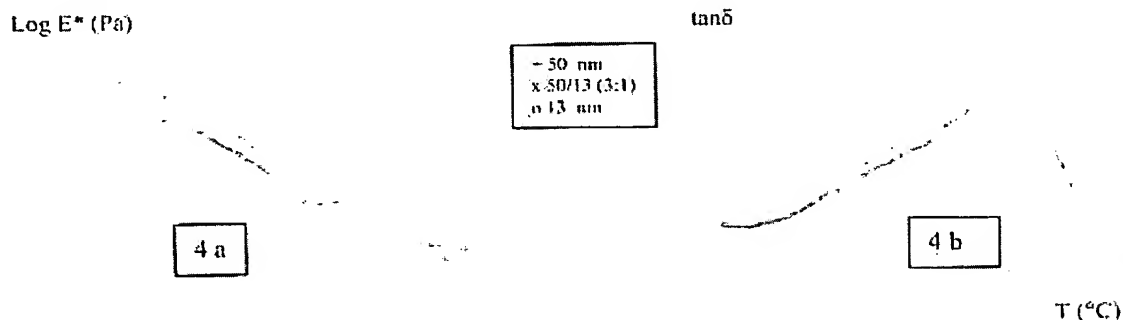   T (°C)

Figure 4: Effect of size distribution a) Log E* vs T   b) tanδ vs T

We already mentioned that volume and size ratios of large to small particles are key parameters which control packing density. For hard spheres, maximum density is obtained when the small particles are packed to their maximum density within the voids of the large spheres: at 75/25 weight ratio with increasing D_{large}/D_{small} =10. An 85% solid content could be in theory be obtained through these conditions [13].
When looking at the DMTA curves (figures 4a,4b) , one can notice a upper shift of plots Log E* versus T for all coatings formulated with mixtures of particles compared to the ones containing 13 or 50 nm particles. The loss tangent is found maximum (tanδ= 0.135) with the 75/25 wt ratio of D_{50nm}/D_{13nm} . This result is in agreement with the packing density theory.

2.2 Abrasion and gloss *(table 2)*

Results from abrasion test do not show any maximum. Resistance to abrasion is best with the 50 nm silica coating. In contrast, gloss values increases with mixtures rich with 13 nm particles. A good compromise is the use of a 3/1 mixture of 50/13 nm particles for which gloss is maintained while abrasion stays at an acceptable level.

In order to analyze correctly the results, one should not forget that abrasion and gloss are surface properties while viscoelastic measurements are related to bulk properties.

3 Effect of silica concentration *(table3)*

Silica loading in the coating is raised from 0 to 40% SiO_2

FORMULATION *	Standard	4	5.	6	7
Code	Reference	Si 20/D3(1)	Si 25/D3(1)	Si 30/D3(1)	Si 40/D3(1)
SiO_2 (% wt)	0	20	25	30	40
HDDA (g)	86	46.4	35.9	27.4	
PEA (g)	14	11.3	10.4	9.6	
HOG 103-31 (g)		--		--	
Lab 103-32 (g)		--		--	
HOG 103-53 (g)		42.3	53.7	63	
Results					
Log (E*) (-50°c) Pa	9.09	9.06	9.09	9.15	9.27
Tg °C	86	89	88	88	83
Tan δ (at Tg)	0.12	0.140	0.122	0.120	0.116
Log (E*r) (150°c) Pa	8.06	8.10	8.16	8.24	8.40
Gloss (60°)	85	80	77	72	69
Abrasion %	28	7	4	4	5

Table3 : Formulation and Coating properties. Effect of silica loading

3-1 Dynamic mechanical properties *(figure 5)*

Log E* (Pa)   tanδ

+ 20% 50 nm
X 30% 50 nm
O 40% 50 nm

5a   5b

T (°C)
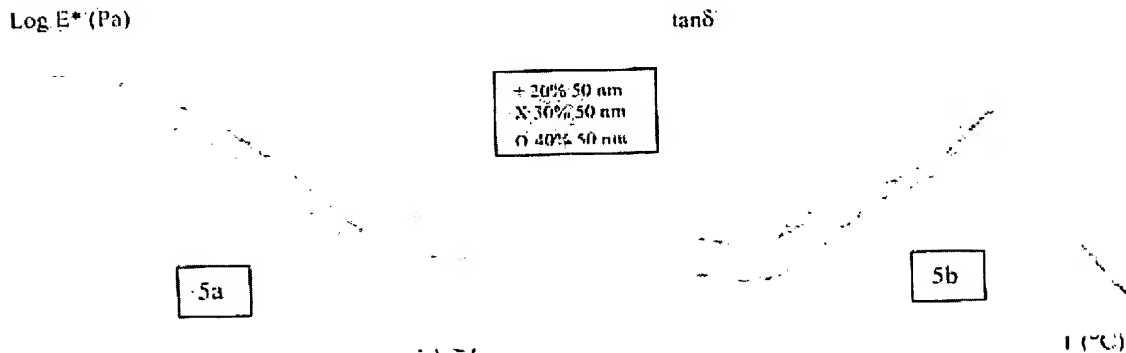
Figure 5:   Effect of SiO2 content a) Log E* vs T   b) tanδ vs T

When the SiO_2 loading is increased, we detected an upper shift of $Log\ E^* - T$ curves in the whole temperature range. For non interacting rigid fillers in plastics, it is known that the elastic modulus E is independent of particle size and size distribution. It increases with volume fraction of filler. An empirical and useful formulae has been proposed by Eilers (22):

$$Ee/Eo = [1+1.25\phi/(1-\phi/\phi_{max})]^2$$

(Ee/Eo is the relative elastic modulus of the composite and the polymer; ϕ the volume fraction of the filler and ϕ_{max} the maximum packing volume fraction, $074<\phi_{max}<0.8$). Other similar relations are proposed [23,24].

We plotted in figure 6 the relative modulus E^*_{rel} ($150°C$) = $E^*_{composite}/Eo^*_{reference}$, taken at the rubbery plateau against ϕ (silica volume fraction) along with Eilers' equation ($\phi_{max}=0.74$)
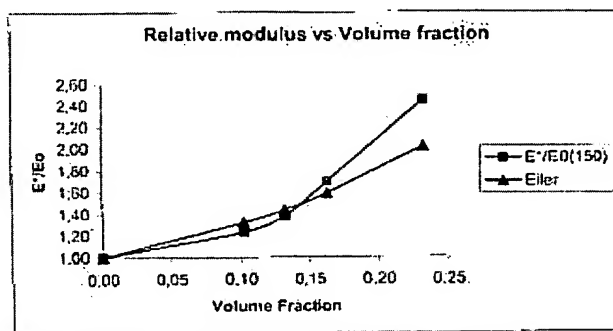

Figure 6: Effect of volume fraction (ϕ) on relative moduli (E^*/Eo)

At ϕ <12%, within experimental errors, the experimental curve follows Eilers' equation with an identical slope. The hard and well dispersed particles behave then as non-interacting hard spheres.
At ϕ >12%, the experimental curve shows a steeper slope, indicating that strong interactions occur at the silica-polymer interface or between particles. We can therefore expect that some physical properties are enhanced at a lower loading than for traditional nonreactive fillers.

3-2   Abrasion resistance and gloss (table 3)

We mentioned in section 1 that particles of 50 nm bring higher resistance to abrasion than small 13 nm particles. The effect of SiO_2 loading are therefore investigated only with 50 nm particles. Results from Taber abrasion test show that abrasion resistance is best when SiO_2 loading is around 25-30%. Gloss decreases when SiO_2 loading increases.

CONCLUSIONS

- Properties of thin UV-cured nanocomposite coatings of HDDA/PES = 84/16 w/w containing 0 to 40% weight of 13, 25 and 50 nm silica particles were compared in this study.
- The hybrid organic-inorganic coatings show superior mechanical and surface properties than the reference organic coating.
- Strong interactions at the inorganic-organic interface and between silica particles are found starting from 15% silica loading.
- Complex modulus E^* increases and loss tangent decreases with higher silica content and smaller particle size.
- Mixtures 75/25 weight ratio of 50/13 nm gave highest values of E^* and $tan\delta$. This is consistent with maximum packing theory with blends of large and small particles.
- Abrasion resistance is best with 50 nm size while gloss is highest with 13 nm particles.
- Friction is lowest with the 50 nm coating and is correlated to abrasion resistance.
- AFM observation shows a bumpy surface for the 50 nm coating which limits physical contact with the abrasion rolls.

Thus, Highlink OG acrylic grades developed by Clariant are definitely efficient products which improve significantly surface and bulk properties of UV-cured thin coatings.

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